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Electrical and Electrochemical Properties of TiO_2 Films Grown by Organometallic Chemical Vapour Deposition

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The electrical and photoelectrochemical properties of TiO_2 films, which were obtained by the vapour decomposition of ethyl titanate, are described. The electrical properties depend mainly on the deposition temperature. Films deposited at high temperatures have much lower electrical conductivity but remarkably higher photosensitivity than those deposited at low temperatures. The deposition temperatures are found to affect the electrochemical properties, such as anodic photocurrent-potential characteristics and spectra dependences of anodic photocurrents. Some doping effects of Al, Cr and Fe on the both properties are also examined.

In a previous paper¹ we described briefly the electrical and electrochemical properties of titanium dioxide (TiO_2 , rutile and anatase) films grown by the vapour decomposition of ethyl titanate. The as-grown films behave as a typical n-type semiconductor and have moderate electrical conductivity and large photoconductivity at room temperature without any additional treatment, such as reduction or heating following the deposition.

TiO_2 is a stable photoanode, but can respond only to light which has a larger energy than its band gap ($E_g = 3.0 \text{ eV}$), limiting its utility in an electrochemical photocell or in photocatalysis. Doping with various elements improves the response to ultraviolet or visible light.²⁻⁴ We describe in this paper the details of an electrical and photoelectrochemical study of TiO_2 films obtained by our method, along with the effect of doping on the electrical and photoelectrochemical properties.

EXPERIMENTAL

The apparatus for the deposition of TiO_2 films and the starting complex, ethyl titanate, used in this study were the same as those reported previously.¹ Commercial reagent-grade isopropyl titanate was also used as a starting complex. Doping experiments were performed by the introduction of the vapour of aluminium isopropoxide, or iron or chromium acetylacetonate. The former two complexes are commercial samples, and the latter was prepared according to a literature method.⁵ The dopant complexes were transported by nitrogen gas into the furnace and mixed with ethyl titanate vapour at the entrance to the reaction furnace. The substrate, consisting of a glass sheet (Corning no. 7059) and a titanium plate, was treated in the same way as in the previous study.¹

The electrical and electrochemical properties of the TiO_2 films were examined by the same method as described previously.¹ The electrolyte used for the electrochemical measurement was

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0.1 mol dm⁻³ Na_2SO_4 solution, unless otherwise specified. The reference electrode was a saturated calomel electrode (SCE). All potentials are given in V vs. SCE. A 500 W Xe lamp and a fluorescent lamp were used as a light source for the photoelectrochemical study and photoconductivity measurements, respectively. Monochromatic light was obtained using a monochromator (Nikon G-250) from the 500 W Xe lamp. The gases used were purified by passing them through active copper and phosphorous pentoxide.

RESULTS AND DISCUSSION

ELECTRICAL PROPERTIES OF TiO_2 FILMS ON THE GLASS

The electrical properties of TiO_2 films deposited on a glass substrate from ethyl titanate depend on the deposition conditions, especially the substrate temperature. Some examples of the data obtained are listed in table 1. The deposits obtained at 400-440 °C (hereafter referred to as lower temperatures) have a larger conductivity than those at 470-500 °C (higher temperatures) while the conductivity of the latter

TABLE 1.—DEPOSITION CONDITIONS AND RESISTIVITY OF TiO_2 FILMS

sample number	96	103	72	80
substrate temp./°C	420	500	470	470
N_2 flow rate/cm ³ s ⁻¹	0.60	0.60	0.80	1.00
O_2 flow rate/cm ³ s ⁻¹	0.30	0.30	0.20	0
film thickness/ μm	0.80	0.90	1.00	0.79
rutile content (%)	62	0	0	1
resistivity/ Ω cm				
in H_2	2.5×10^3 (1.7×10^3) ^a	2.6×10^3 (2.5×10^3)	4.0×10^3 (1.3×10^3)	4.6 (3.3)
in N_2	2.8×10^3 (2.2×10^3)	3.6×10^3 (4.6×10^3)	4.4×10^3 (2.2×10^3)	6.6 (3.6)
in Ar	1.9×10^3 (6.2×10^3)	5.3×10^3 (2.6×10^3)	6.2×10^3 (1.1×10^3)	6.6 (3.3)
in O_2	3.3×10^3 (2.5×10^3)	1.5×10^3 (4.0×10^3)	6.6×10^3 (1.3×10^3)	7.6 (6.6)

^a Resistivity values in parentheses are those under illumination.

increases by 10^4 under illumination even by a weak fluorescent light (light intensity, 0.6 mW cm⁻²). Exposure of the films to atmospheric gases also affects the conductivity. This effect is more notable under illumination than in the dark. The fact that the reducing gas, H_2 , increased the conductivity (especially under illumination) is consistent with the properties of an n-type semiconductor.¹⁰ The films deposited at lower temperatures had little photoactivity, probably indicating the existence of donors at such shallow levels as to be excited into the conduction band by thermal energy at room temperature. The films grown in the absence of additional oxygen gas have larger electrical conductivity owing to a drastic deviation of the stoichiometry, which was confirmed by a weight increase when oxidized in air, and had very little photoresponse. The TiO_2 films obtained from isopropyl titanate tended to have a very low conductivity (10^{-11} Ω^{-1} cm⁻¹).¹¹

The photoresponse of the high-temperature deposits is large, as described above, but the response rate was unexpectedly slow. A typical example of the

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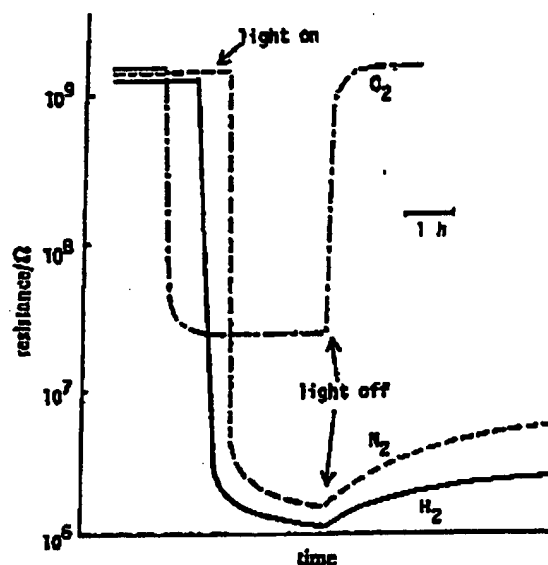


FIG. 1.—Photoresponse in the electrical resistance of a TiO_2 film (no. 103) under an atmosphere of H_2 , N_2 and O_2 gases (for deposition conditions see table 1).

time dependence of the photoresponse in various gases is shown in fig. 1. When the sample was illuminated, the resistivity decreased sharply in the initial stages and the rate of decrease became slower. 2–3 h later the resistivity levelled to a minimum value that was dependent on the type of atmospheric gas used. On the other hand, when the light was turned off, the change in resistivity was much slower, especially under hydrogen, nitrogen or argon. The resistivity measured after the d.c. ohmmeter was detached for a short while or when the polarity was reversed was still consistent with that assumed by extrapolating the transient curves or that obtained before changing the polarity, suggesting strongly that the charge carrier is not ionic but electronic. The very slow response on turning off the light tells us that the carriers which were generated under illumination have a long lifetime even in the dark. This process cannot be explained by a simple physical mechanism, but rather in terms of a chemical surface reaction of the films with the atmospheric gas (an adsorption-desorption process). Hydrogen is thought to diffuse into the TiO_2 crystal, donating an electron by ionization in the lattice.^{24,25} There have been no reports of such behaviour for nitrogen: traces of hydrogen in the gas may play a role. In contrast to the case of hydrogen or nitrogen, the response in oxygen is low but very fast, as shown in fig. 1, indicating that the reaction between the film surface and the atmospheric oxygen can be rapidly equilibrated, including deprotonation.²⁵

Doping with aluminium, chromium or iron had a slight effect on the dark- and photo-conductivities, but the essential features of both conductivities were the same as for undoped films, as shown in table 2. Note, however, that the response rate when the light was turned on and off is enhanced by the aluminium doping, as shown in fig. 2. We have no clear explanation of this doping effect at present, but more detailed studies may enable us to find a suitable composition of the films for them to work effectively as a gas sensor.

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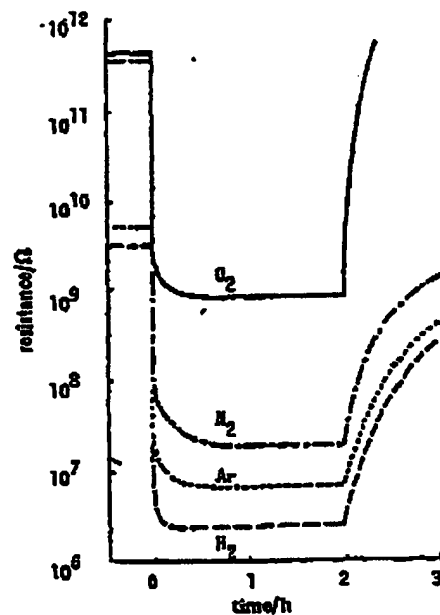
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sample number	216	234	253	293	294
dopant	Al	Al	Cr	Fe	Fe
substrate temp./°C	435	480	435	415	470
N ₂ flow rate/cm ³ s ⁻¹	0.6	0.6	0.6	1.1	1.1
film thickness/μm	1.3	1.4	0.86	3.9	3.3
rutile content (%)	100	0	100	0	0
resistivity/Ω cm					
in H ₂	2.0 × 10 ⁹ (1.5 × 10 ⁹)*	1.9 × 10 ⁸ (1.3 × 10 ⁸)*	1.7 × 10 ⁸ (9.9 × 10 ⁷)	1.7 × 10 ⁸ (1.4 × 10 ⁸)*	1.7 × 10 ⁸ (1.1 × 10 ⁸)
in N ₂	5.0 × 10 ⁹ (2.0 × 10 ⁹)*	2.4 × 10 ⁷ (9.1 × 10 ⁶)*	4.0 × 10 ⁸ (1.3 × 10 ⁸)*	7.5 × 10 ⁸ (3.6 × 10 ⁸)*	4.4 × 10 ⁸ (1.7 × 10 ⁸)
in Ar	5.4 × 10 ⁹ (1.8 × 10 ⁹)*	2.4 × 10 ⁸ (3.1 × 10 ⁸)*	3.1 × 10 ⁸ (1.1 × 10 ⁸)*	6.6 × 10 ⁸ (1.1 × 10 ⁹)*	1.8 × 10 ⁸ (1.5 × 10 ⁸)*
in O ₂	4.5 × 10 ⁹ (7.2 × 10 ⁹)*	2.4 × 10 ⁷ (4.1 × 10 ⁶)*	4.3 × 10 ⁸ (2.9 × 10 ⁸)*	1.2 × 10 ⁹ (1.7 × 10 ⁹)*	1.1 × 10 ⁸ (1.5 × 10 ⁸)*

* Resistivity values in parentheses are those under illumination.

FIG. 2.—Photoreponse in the electrical resistance of an Al-doped TiO₂ film (no. 234) under an atmosphere of H₂, N₂, Ar and O₂ gases (for deposition conditions see table 2).

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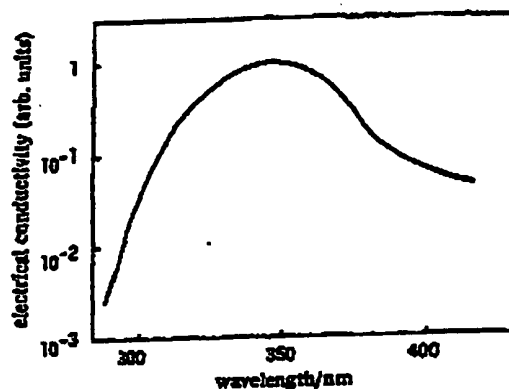
 7×10^4 1×10^5 4×10^4 7×10^4 8×10^4 5×10^5 $\times 10^6$ 5×10^7 

FIG. 3.—Spectral dependence of the photoconductivity of a TiO_2 film (no. 72) (for deposition conditions see table I). Data were not corrected for light intensity.

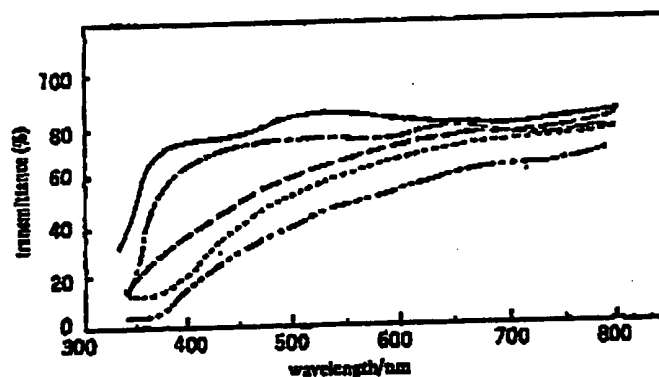


FIG. 4.—Visible absorption spectra of TiO_2 films: (—) no. 72, (---) no. 94, (— · —) no. 96, (— · —) no. 103, (·····) no. 139. Deposition conditions: no. 72, 96 and 103, see table I; no. 94, substrate temperature 390°C ; no. 139, substrate temperature 420°C , from isopropyl titanate.

The spectral dependence of photoconductivity measured in air using the Xe lamp as a light source is shown in fig. 3. Maximum response is observed at 350 nm, namely at the intrinsic region as expected. However, the photoconductivities shown in tables 1 and 2 are those obtained under illumination by white light from a fluorescent lamp. Therefore, some deeper extrinsic levels might also contribute to the photoconductivity.¹⁸

The difference between low-temperature deposits and those at high temperature is clearly shown in the visible-light absorption spectra (fig. 4). The deposits at higher temperatures showed a clear absorption edge around 400 nm, which is consistent with the photoconductivity data in fig. 3. The low-temperature deposits had no clear absorption edge, indicating that there are many trap levels in the forbidden region.

The temperature dependence of the resistivity (20–200 $^\circ\text{C}$) of the films obtained at higher temperatures suggested the band gap to be 3.0–3.3 eV. For the low-temperature

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deposits on the other hand, the activation energy of conduction is as low as 0.3 eV, indicating the existence of shallow traps.

ELECTROCHEMICAL PROPERTIES OF TiO_2 FILMS ON TITANIUM PLATE

As reported previously,¹ the TiO_2 films obtained with our method behave as typical n-type semiconductor electrodes in a photoelectrochemical cell. The characteristics of the anodic current against potential were found to depend strongly on the deposition conditions, in particular on the deposition temperature. The general features observed in 0.1 mol dm⁻³ Na_2SO_4 solution can be summarized as follows: (1) The films deposited at lower temperatures exhibit large anodic photocurrents which are saturated at a rather positive potential (ca. 0.5 V vs. SCE). (2) The films deposited at higher temperatures showed rather small photocurrents which are saturated at a considerably negative potential (ca. 0 V vs. SCE). (3) Anodic dark currents are negligibly small in every case. (4) The deposits are stable against photocorrosion. (5) The deposits at an optimum condition have a high quantum efficiency for anodic photocurrent, comparable to that of single crystals.

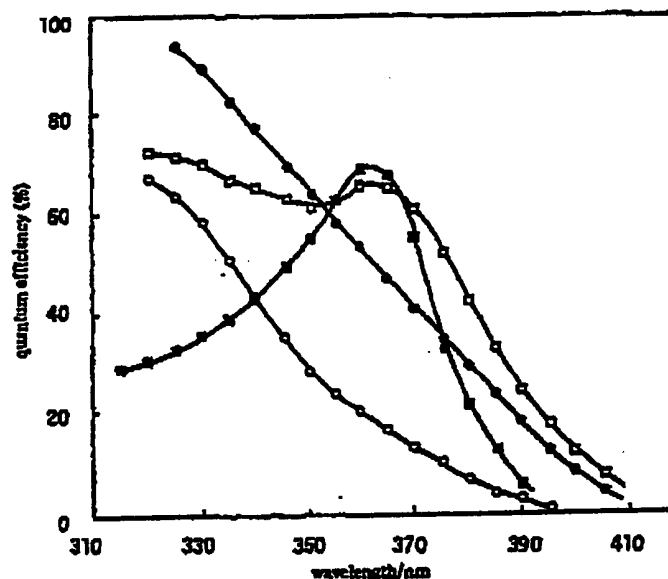


Fig. 5.—Spectral dependence of the quantum efficiency for the anodic photocurrents of TiO_2 film electrodes: O, no. Ti-04; ●, no. Ti-10; □, no. Ti-12; ■, no. 169. The anodic photocurrents were measured at 0.5 V vs. SCE in 0.1 mol dm⁻³ Na_2SO_4 solution. Deposition conditions: no. Ti-04, Ti-10 and Ti-12, see ref. (1); no. 169, substrate temperature: 470 °C, from isopropyl titanate.

Thus these results indicate that the as-grown films have excellent properties as photoanodes. The decomposition temperature also affected the spectral dependence of the quantum efficiency for anodic photocurrents, as shown in fig. 5. Raising the deposition temperature leads to an improvement in the response at longer wavelengths.¹ A pure anatase film obtained at 420 °C from isopropyl titanate¹¹ had a maximum response at ca. 365 nm, which is very close to that of the deposits at high temperatures

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from ethyl titanate. The film showed a very low conductivity as described above. Therefore it may be suggested that the spectral dependence of the photocurrent is closely related to the electrical properties of the films. An estimation of the donor concentration in the deposits may clarify the relation. A Mott-Shottky plot is one possible way to obtain such an estimation. We then measured the differential capacitances of these film electrodes in an aqueous electrolyte in the usual manner. However, we could not obtain a meaningful result, since the capacitance (C) measured depended strongly on the frequency (0.1–10 kHz) of the signal used in the impedance bridge, and the plot of $1/C^2$ against potential gave a straight line for one sample but not for another.

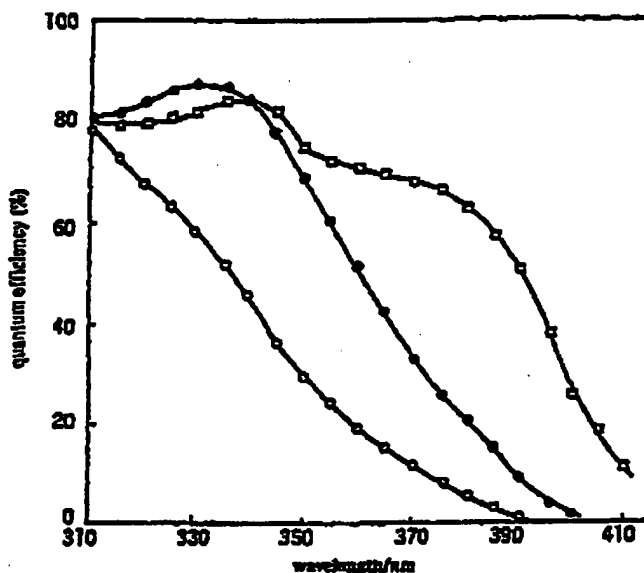


FIG. 6.—Effect of Fe- and Al-doping on the action spectra for anodic photocurrents: \square , Fe-doped (no. 299); \bullet , Al-doped (no. 238); \circ , undoped (no. 230). The anodic photocurrents were measured at 0.8 V vs. SCE in 0.1 mol dm⁻³ Na₂SO₄ solution. Substrate temperature: no. 230 and 238, 435 °C; no. 299, 440 °C.

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The doping effects of aluminium and iron on the spectral dependence of the anodic photocurrent are shown in fig. 6, where only the results obtained at optimum doping conditions are shown. The dopant concentrations were too low (perhaps ca. 1% or so) to be measured precisely with our energy-dispersion type of EPMA. For reference the result on an undoped film, obtained under the same deposition conditions as the doped one, is also shown in fig. 6. By doping with aluminium, the spectral response can be appreciably extended. However, on comparing fig. 6 with the result in fig. 5, it is clear that the spectral dependence of the aluminium-doped film is similar to that of an undoped film at a higher temperature (470 °C). Therefore, we conclude that aluminium doping is not essential to extend the spectral dependence, in agreement with the observations of other workers.^{4,5} On the other hand, iron doping has such a remarkable effect that a higher quantum efficiency (η) is observed even at longer

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wavelengths (25% at 400 nm and 0.7% at 500 nm). Interestingly this film is composed of 100% anatase.

Chromium doping has been reported to be effective in extending the spectral response.^{2,4,5} However, in our case no such optimum doping conditions were found: doping with chromium suppressed the anodic photocurrents. These findings suggest that the doping conditions must be carefully examined, and that the doping effect may depend on properties of the original undoped samples.

As mentioned above, the i against V characteristics of TiO_2 films can be controlled by the deposition temperature. A negative onset potential and sharp current rise on sweeping the potential are observed for films obtained at high temperatures. The film obtained from isopropyl titanate behaved similarly. If a film having such good i against V characteristics is used as a photoanode in a photovoltaic cell, the cell can be expected to have good current-voltage characteristics, namely a high fill factor. Therefore, we examined the output power characteristics of the cell, in which no. 169 film and platinum were used as the photoanode and photocathode, respectively. A single-compartment cell system was employed, with $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ or

TABLE 3.—OUTPUT POWER CHARACTERISTICS OF ELECTROCHEMICAL PHOTOCELL, TiO_2 (NO. 169)/ELECTROLYTE/Pt

electrolyte	$0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$	$0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{PO}_4$	$0.1 \text{ mol dm}^{-3} \text{ NaOH}$
open-circuit voltage/V	0.44	0.81	0.78
short-circuit current/ mA cm^{-2}	1.02	1.01	0.96
maximum output power/ mW cm^{-2}	0.089	0.46	0.50
fill factor	0.20	0.56	0.67
$\phi\%$ ^a	0.089	0.46	0.50

^a Maximum power conversion efficiency. Light intensity, 100 mW cm^{-2} .

$0.1 \text{ mol dm}^{-3} \text{ NaOH}$ solution without intentional addition of any redox couple was used as an electrolyte. The results obtained are shown in table 3. The cell,



has a very high open-circuit voltage, V_{oc} , and a large fill factor of ca. 0.6–0.7. The light-electricity conversion efficiency (ϕ) was 0.5% under white-light illumination. Both V_{oc} and ϕ are comparable to the values (0.8 V and 0.5%) observed for a two-compartment cell system



The high efficiency observed may be ascribed to the high fill factor as well as to the high value of V_{oc} . Good i against V characteristics of the film (no. 169) used contribute to the high fill factor.

In order to clarify the unexpectedly high value of V_{oc} , the rest potentials of the TiO_2 and Pt electrodes were measured in the dark and under illumination. The data are listed in table 4. The potential of the TiO_2 electrode varied in the usual manner by ca. 60 mV per pH unit according to the Nernst equation,²⁵ whereas that of the Pt electrode was less sensitive to any variation of pH. The difference between the pH dependences of both electrodes should be the reason why the high value of V_{oc} was

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TABLE 4.—REST POTENTIALS (V vs. SCE) OF TiO₂ ELECTRODE (NO. 169) AND Pt ELECTRODE

electrolyte	0.1 mol dm ⁻³ Na ₂ SO ₄ (pH 7)	0.1 mol dm ⁻³ Na ₂ PO ₄ (pH 12)	0.1 mol dm ⁻³ NaOH (pH 12)
TiO ₂	-0.30 (-0.54) ^a	-0.73 (-0.93)	-0.70 (-0.92)
Pt	+0.15 (+0.15)	-0.15 (-0.15)	-0.07 (-0.07)

^a Potential values in parentheses are those under illumination.

observed. Table 4 also indicates that the cell has a large dark e.m.f. (ca. 0.45–0.55 V depending on the pH of the solution), which was not always reproducible. Therefore, the net V_{oc} induced by photon energy may be estimated to be 200–250 mV, which was comparable to the value (ca. 200 mV) found for a polycrystalline TiO₂-based cell.¹⁶ We cannot clarify at present the reason why there exists such high dark e.m.f., although it may be supposed that dissolved oxygen plays an important role. On the Pt electrode no gas evolution was observed, unlike the TiO₂ electrode, on which O₂ gas evolution took place. The potential of the Pt electrode (–0.07 V vs. SCE in 0.1 mol dm⁻³ NaOH, pH 12) seems to be far more positive than that of the H⁺/H₂ couple (ca. –0.95 V vs. SCE, pH 12) and more negative than that of the O₂/OH[–] couple (ca. 0.25 V vs. SCE, pH 12). Therefore, the actual cathodic reaction mainly occurring on the Pt electrode may be concluded to be the reduction of O₂ gas in solution. The fact that bubbling N₂ gas around the Pt electrode reduced the value of V_{oc} by ca. 0.2 V supports this conclusion. The report that the cell

TiO₂/5 mol dm⁻³ NaOH/O₂, Pt

had $V_{oc} = 0.89$ V,¹⁷ and other reports on the effect of oxygen gas,^{18,19} are likely to confirm our observations.

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